Preparation of Glycoether Lignin from Sugi (Cryptomeria japonica D. Don) Woodmeal by Acid-Catalyzed Solvolysis and Preparation of Heat-Resistant Polyester from the Glycoether Lignin

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Abstract
Preparation of glycoether lignin from Sugi (Cryptomeria japonica D. Don) woodmeal by acid-catalyzed solvolysis in 2-phenoxyethanol has been performed. The glycoether lignin had the hydroxyl content of 0.677 mmol/g and average molecular weight of $2.5 \times 10^3$. The glycoether lignin showed good solubility to various common organic solvents, such as methanol, ethanol, acetone, 2-butane and chloroform. Crosslinked glycoether lignin, obtained by esterification with adipoyl chloride in acetone, showed thermal stability up to 230 °C.

Key-words: Glycoether lignin, Acid-catalyzed solvolysis, Polyesters

1. Introduction
Utilization of wooden biomass as feedstock for functional materials is attracting increasing attention in terms of suppression of carbon dioxide emission and development of alternatives to petroleum resources. Considering the major components of wooden biomasses, i.e. cellulose, hemicelluloses and lignins, cellulose has long been utilized for plastic materials after derivatization. Recently, novel cellulose utilization as soft materials or development of novel composites after nanofibrillation has been proposed. Hemicelluloses have also been utilized as food additives and commodity chemicals. Not limited to these conventional uses, plasticization of hemicelluloses by derivatization is also proposed. Lignins prepared by various physical and/or chemical methods also have a potential as an alternative for conventional petroleum resources, because lignins have the largest quantity as non-petroleum aromatic substances in the wooden biomasses.

Although enormous amounts of denatured lignins can be obtained as a byproduct of pulp processing in papermaking industry, main purpose of the current lignin production is to provide fuel for the papermaking process. On the other hand, the usage of industrially produced lignins, such as Kraft lignin or lignin sulfonate, is limited to specialized purposes such as mortar thickener and soil modifier. The reason for the limited use of lignin mainly lies in the complexity of the molecular structure of lignin and in the poor solubility in common organic solvents.

Organo-soluble lignins can be prepared by ethanolation or steam explosion. However, the production of organo-soluble lignins is limited to laboratory level, because these processes have challenges regarding safety management of the processes. The challenges come from the usage of highly flammable ethanol or necessity of devices durable to high temperature and pressure.

In order to prepare organo-soluble lignins as raw materials for production of various chemicals by overcoming the above-mentioned problems, usage of various low-volatile solvents as extraction media has been investigated. Funaoka et al. have investigated the preparation condition of lignophenols by using mixture of 72% (w/w) sulfuric acid and p-cresol as preparation media. Kubo et al. have prepared glycol lignin in a mixture of cyclic carbonate and ethylene glycol containing catalytic amount of sulfuric acid. In these preparation systems, p-cresol and ethylene glycol are incorporated to the backbone of lignin and act as polar functional groups enhancing solubility to preparation media.

We have focused on glycol ether-type organic solvents, such as 2-phenoxyethanol (2-PhETOH) and ethylene glycol monobutyl ether (EGMBE) as novel lignin preparation media. This class of solvents have high boiling points of more than 160 °C, miscibility with various common organic solvents.
solvents, and moderate affinity to cellulosic polysaccharides and lignins. On the other hand, hydroxy groups of these solvents are not dissociative enough to cause solvolysis of lignins solely by the solvents themselves. Therefore, catalytic amounts of inorganic acids, such as sulfuric acid, or organic sulfonic acids are required for the preparation. In the present paper, we have investigated the solubilized state of lignin condensates in 2-PhEtOH or EGMBE (referred to as glycolether lignins in the following sections) prepared by using catalytic amount of dodecylbenzene sulfonic acid. Furthermore, we have prepared aromatic polyesters from the lignin condensates by esterification with various dicarboxylic acid chlorides. We also report the thermal properties of the glycolether lignin polyesters.

2. Materials and methods

2.1 Preparation of Glycolether Lignin Condensate

In a 300-mL double-necked flask equipped with thermometer and condenser placed on magnetic stirrer, 10 g of 65 mesh-passed wood meal of Sugi (Cryptomeria japonica D. Don), 10 g of 2-PhEtOH, 85 g of EGMBE, and 0.663 g (2 mmol) of dodecylbenzenesulfonic acid were mixed at 160 °C for 2 h. After cooled to the ambient temperature, the solvolysis product was collected by suction filtration using No.2 filter paper. Solid residue on the Buffin funnel was washed with diethyleneglycol monoethyl ether (DEGMEE) and 2-butanone (100 ml each). The filtrate of reaction mixture, mixed with the wash liquid, was condensed at 120 °C for 3 h to obtain 47 g of the glycolether lignin condensate.

2.2 Characterization of Glycolether Lignin

Glycolether lignin was firstly assessed for the solubility in various common organic solvents. Based on the results of solubility test, characterization of glycolether lignin in the solvated state was performed by the following methods: FT-IR analysis, liquid film method on KBr with the resolution of 4 cm⁻¹ by using Horiba FT-720 spectrometer (Horiba Corporation, Kyoto, Japan); molecular weight distribution by gel permeation chromatography by using HLC-8020 chromatograph (Tohos Corporation, Tokyo, Japan) equipped with refractive index detector and GMH HR-M column (7.8 mm i.d. × 300 mm) calibrated by polystyrene standards, to which chloroform was eluted with the flow rate of 0.8 ml/min; ¹H NMR analysis (Avance DPX400, Bruker Biospin, Billerica, MA, USA, solvent: CDCl₃).

2.3 Fractionation of glycolether lignin condensate

Glycolether lignin condensate (47 g) was mixed with 200 ml of 1-butanol / hexane = 1/1 (v/v) and kept at 4 °C overnight. Supernatant and precipitate were separated by centrifugation (9,800 × g, 4 °C, for 5 min). Supernatant was vacuum-condensed by rotary evaporator. Precipitate was washed with 1-butanol and vacuum-dried. Yield of the supernatant and precipitate was 43.5 g and 2.6 g, respectively.

2.4 Esterification of Glycolether lignin with diacid chlorides

To 0.2 g of Glycolether lignin condensate dissolved in 0.3 ml of acetone, dicarboxylic acid chlorides with the corresponding molarity to hydroxy groups in glycolether lignin condensate (0.15 g of adipoyl chloride, 0.28 g of sebacoyl chloride, or 0.15 g of terephthaloyl chloride) and the corresponding amount of triethylamine were added and mixed at 4 °C.

Esterification product, precipitate in acetone, was washed by acetone, methanol, and distilled water. Afterwards, the esterification product was centrifuged (9,800 × g, 4 °C, for 5 min). After the supernatant was decanted, precipitated esterification product was vacuum dried at 50 °C for 1 day. Yield of the product was 0.124 g (62.2%).

Characterization of the esterification product was performed by FT-IR (Horiba FT-720), observation of phase transition behaviour by hotstage-equipped optical microscopy (Nikon ECLIPSE 50i POL polarized optical microscope, Nikon Corporation, Tokyo, Japan), equipped with Linkam 10013L hotstage (Linkam Scientific Instruments, Tadworth, UK), heating rate of 10 K/min, and thermal degradability by differential scanning calorimetry (DSC, DSC-8230, Rigaku Corporation, Tokyo, Japan).

3. Results and discussion

3.1 Properties of Glycolether Lignin Condensate

The obtained glycolether lignin condensate had an appearance of dark-brownish tar-like liquid. Glycolether lignin condensate was fully soluble in methanol, ethanol, acetone, 2-butanol and chloroform, partially soluble in ethyl acetate, but insoluble in hexane toluene, 1-butanol, and 2-propanol. Hydroxyl content of glycolether lignin condensate, estimated by titration of released acetic acid after acetylation, was 38 mg/g (0.677 mmol OH/g).

3.2 Molecular weight Distribution of Glycolether Lignin Condensate and Its Fractions

Fig. 1 shows elution profiles of glycolether lignin condensate and its fractions. Each elution profiles are mainly composed of two regions. While the region 1 contains broad elution peak, the region 2 contains sharp peaks with positive or negative polarities. The broad peak in the region 1 originates from the polymeric components in the condensate. The negative peaks in the region 2 (the components with relatively smaller refractive indices than chloroform) are attributed to solvent species in the reaction medium. Therefore, the regions 1 and 2 are mainly composed of glycolether lignin and residual solvents, respectively. While condensate and soluble fraction are mainly composed of the
residual solvents, insoluble fraction are mostly composed of glycolether lignin. Therefore, prepared glycolether lignin is mainly contained in the insoluble fraction in 1-butanol / hexane = 1 / 1 (v / v) fraction. From the elution profile, glycolether lignin has the weight-averaged molecular weight and polydispersity index of $2.5 \times 10^3$ and 1.3, respectively.

**Fig. 2** shows FT-IR spectrum of glycolether lignin condensate and its fractions. From the spectra, wavenumbers of the absorptions and their assignments and origins are summarized in Table 1. Most of the peaks in the soluble fraction are assigned to 2-PhEtOH, showing that the major component of the soluble fraction is 2-PhEtOH. While many peaks were overlapped by the peaks from 2-PhEtOH, absorptions inherent to glycolether lignin were observed at 857 (out-of-plane deformation of guayacyl C-H), 1,083 (C-O deformation of secondary alcohols), 1,213 (stretching of C-C and C-O in lignin), 1,510 (aromatic ring deformation), 2,864 (stretching of methoxy C-H), 2,923 (C-O-C stretch) and 3,416 cm$^{-1}$ (O-H stretch). This shows that the insoluble fraction contains glycolether lignin.

**Fig. 3** shows ¹H NMR spectrum (in CDCl₃) of glycolether lignin precipitated in 1-butanol / hexane = 1 / 1 (v / v). Most of the observed peaks in the spectrum (peaks with the asterisks) were assigned to 2-PhEtOH, EGMBE, and DEGMEE. These solvent components remain unreacted with the glycolether lignin, as suggested from the relatively narrow peak width of these solvent species. The glycolether lignin-related broad peak assigned to methoxy protons was observed between 3.2 to 4.3 ppm. Aromatic peak assigned to glycolether lignin was observed between 6.6 and 7.2 ppm as a satellite peak to solvent-assigned peaks.

### 3.3 Glycolether lignin polyester

**Fig. 4** shows FTIR spectrum of the esterification product of glycolether lignin, precipitated in 1-butanol / hexane = 1 / 1 (v / v), with adipoyl chloride. Hydroxy stretching peak, observed at 3,422 cm$^{-1}$ in the spectrum of glycolether lignin, considerably decreased in the esterification product. On the other hand, ester C=O and C-O stretching peaks appeared at 1,752 and 1,039 cm$^{-1}$, respectively. These results show the formation of ester bonds between glycolether lignin and adipoyl chloride.

The esterification product was obtained as the precipitate in

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![Fig. 1](image1.png)

**Fig. 1** GPC elution profile of (a) glycolether lignin condensate and its (b) soluble and (c) insoluble fractions in 1-butanol / hexane = 1 / 1 (v / v). 1: Glycolether lignin; 2: Residual solvents.

![Fig. 2](image2.png)

**Fig. 2** FT-IR spectrum of glycolether lignins fractionated in 1-butanol / hexane = 1 / 1 (v / v). Upper: soluble fraction. Lower: Insoluble fraction. Peaks with asterisks in the spectrum of the insoluble fraction are assigned to 2-phenoxyethanol.
reaction mixture using acetone as the medium. Considering that the glycolether was soluble in acetone, adipoyl chloride reacted as the crosslinker of the glycolether lignin, resulting in the precipitation. The esterified product was easily collected by filtration.

Fig. 5 shows DSC thermogram and polarized optical micrographs at 30, 180, and 220 °C of the glycolether lignin polyester. DSC thermogram showed no distinct transitions, i.e., glass transition and/or melting transition. This suggests that the molecular motion of the polyester is restricted by adipoyl group introduced in the polyester as the crosslinker. Polarized optical micrographs also showed no distinct changes in visual appearances. Although the detailed gravimetical changes were not investigated, the polyester remained almost unchanged after heating up to 230 °C. This suggests the high heat resistance of the glycolether lignin polyester, which offers the potential as highly heat-resistant coating applications.

4. Conclusions

Preparation of glycolether lignin with the catalytic
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